

ABSTRACT

The growth and properties of Methane Sulphonyl Morpholine (MSM) organic single crystal, is reported. MSM crystals were grown by Conventional and Sankaranarayanan-Ramasamy (SR) method. The grown crystals have been characterized for their structural, optical, mechanical, dielectric, laser damage threshold, Photo acoustic, thermal and NLO properties. The results of Conventional and SR method have been compared. It has been observed that the SR method grown crystal have enhanced properties throughout the studies and this observation revealed improved quality of the crystals that give a positive approach towards NLO applications

KEYWORDS: Growth from solution, Non linear optical material, Laser Damage threshold, Photo acoustic analysis.

I. INTRODUCTION

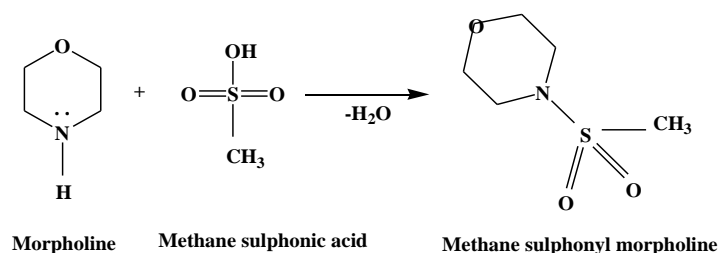
The design, synthesis and characterization of nonlinear organic materials have been motivated by their tremendous potential applications including second-harmonic generation (SHG), frequency mixing, electro-optic modulation, optical parametric oscillation, optical bi-stability, etc. [1–3]. The striking advantages of organic materials at the molecular level exhibit large values of molecular hyperpolarizability (β) and have polarizable electrons (e.g., p-electrons) spread over a large distance and also includes their environmental stability, tunable electronic properties, and enhanced mechanical strength [4-5]. Following this approach, a number of materials with good NLO properties have been found in recent years. However, it is difficult to grow desired size of organic crystals with good optical quality for device applications. In this study, efforts were taken to grow large, single crystals from solutions employing conventional and SR method.

From the literature survey, many morpholine derivative NLO materials have been synthesized and investigated [6-8]. However, no research have been reported on the combination of the morpholine and methane sulphonic acid. A. Perales *et al.* [9] have reported the crystalline structure of Methane Sulphonyl Morpholine (MSM) crystal. Herein, we report the bulk growth of MSM single crystal in detail and the growth morphology, optical, chemical etching, mechanical stability, dielectric, photo acoustic, laser damage threshold, thermal behavior and SHG studies.

II. EXPERIMENTAL DETAILS

1. Synthesis and Conventional Growth

Morpholine and Methane sulfonic acid were combined for the synthesis of the Methane sulphonyl morpholine (MSM) single crystals. Equimolar solutions of the two reactants; Morpholine and Methane sulfonic acid were separately prepared in ethanol and methanol respectively. While mixing this solution by continuous stirring white fumes were obtained featuring an exothermic reaction. The reaction scheme and their chemical structures are illustrated in scheme as given below.



The prepared solution was filtered off and allowed to evaporate at room temperature. To enhance the degree of purity the synthesized crystal was recrystallized twice. The well defined MSM single crystals of size 6 mm × 3 mm × 2 mm were harvested from the mother solution at the end of the nineteenth day. The photograph of MSM single crystals and its morphology using WinXmorph is shown in Figure 1 (a) and (b) respectively.

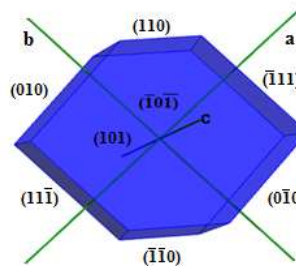


Figure 1 (a) conventionally grown MSM crystal

(b) Morphology of MSM crystal

2.Unidirectional Growth

Good seed crystals grown by conventional method were chosen having a thickness of 2 mm and its morphology analysis reveals that the crystal is developed with eight faces. The face $\langle 101 \rangle$ featuring the plane forming parallel to the c-axis was observed to be quite favorable for the experimental growth. The selected seed was polished well using double distilled water and mounted at the bottom of the ampoule for unidirectional growth. The saturated MSM solution was slowly decanted into the SR growth ampoule without disturbing the seed crystal and placed in the water bath. Suitable temperature was initiated at the top (38 °C) and bottom (32 °C) of the ampoule. The applied temperature at the top controls the spurious nucleation near the surface of the solution, along the length of the ampoule and the excess solute generated by the evaporation of the MSM solution is driven down the ampoule by the temperature gradient. Thus the growth is initiated from the seed fixed at the bottom of the ampoule with driven orientation $\langle 101 \rangle$. Due to the transparent nature of the solution and experimental setup, real time optimization was possible which revealed the solid liquid interface that was found to be flat. After a span of 12-15 days the size of the seed crystal started increasing and the growth system was kept constant for a long period for achieving continuous growth. As a result, MSM crystal of 60 mm length and 20 mm diameter was obtained within 52 days and the cut and polished crystal wafers of MSM crystal is displayed in Figure 2 (a) and (b) respectively.

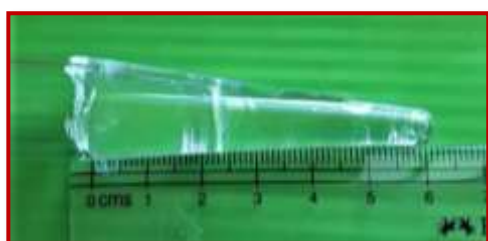


Figure 2 (a) MSM crystal grown by SR method with ampoule

(b) Cut and polished MSM crystals

III. CHARACTERIZATION STUDIES

The conventional and SR method grown MSM single crystals were subjected to various characterization techniques. The Bruker AXS Kappa APEX II CCD diffractometer, equipped with monochromatic MoK α radiation ($\lambda = 0.710 \text{ \AA}$) was used to confirm structural information by single crystal X-ray diffraction analysis and to estimate the unit cell parameter of the grown MSM crystal. Optical transmission window of the crystal was assessed by recording UV-Vis-NIR spectrum using Perkin-Elmer Lambda-35 spectrophotometer. Photoluminescence spectrum was recorded to detect the emission peak using Shimadzu Spectrofluorophotometer RF-5031 PC series with Xenon arc lamp as the excitation source. Chemical etching studies were made to study the distribution of structural defects in the grown crystals using CMM-23 optical trinocular microscope in the reflection mode. In order to determine the mechanical stability of the crystal, Vickers micro hardness measurement was carried out along $\langle 101 \rangle$ plane using Shimadzu hardness tester. The dielectric constant and dielectric loss were measured to investigate the dielectric response of the crystal with varying frequencies at room temperature in the range from 1 KHz to 5MHz using Model PSM 1735 LCR meter. The photoacoustic signal was analyzed by a photo acoustic spectrometer to find out thermal diffusivity of the of the grown MSM crystal. Laser damage threshold analysis was carried out using Q-switched Nd: YAG laser operating at 1064 nm radiation to determine the resistance provided by the crystal to the laser beam. The thermal analysis was carried out in the temperature range of 30–500°C using NETZSCH STA 449F3 analyzer in nitrogen atmosphere at heating rate of 10°C/min to examine the thermal stability. The SHG efficiency has been analyzed by Kurtz-Perry powder technique second harmonic measurement to check the nonlinear response of the crystal to the incident coherent light.

IV. RESULT AND DISCUSSION

1. Single Crystal X-Ray Diffraction

The single crystal XRD analysis confirms that the grown MSM crystal belongs to orthorhombic crystal system with lattice parameter $a=13.103\text{ \AA}$, $b=10.876\text{ \AA}$, $c=5.930\text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$ and the Volume (V) = 778.3 \AA^3 having non-centro symmetry with space group $P2_12_12_1$ which is in good agreement with the reported values [9].

2. UV-Transmittance

From the device point of view the material having higher transparency in the entire UV, visible and near IR region is one of the most desirable properties of the material possessing NLO activity. Optical transmission spectra were recorded for the MSM crystal grown by conventional and SR method. The recorded optical transmission spectra are shown in Figure 3 (a). From the spectra it is observed that conventional and SR method grown MSM crystals have sufficient transparency up to 56 % and 74% respectively in the entire UV, visible and IR region; having lower cut off 242 nm. The reason for improved transparency is that the SR method grown MSM crystal crystallized with reduced scattering from crystal point and line defects. This indicates that the quality is good compared to conventionally grown crystal. Favorable transmittance of the SR method grown crystal in the higher wavelength region suggest its suitability for second harmonic generation or NLO activity. The dependence of optical absorption co-efficient on photon energy helps to study the band structure and the type of transition of the electrons [10]. Optical absorption coefficient (α) was calculated from transmission spectrum using the relation

$$\alpha = \frac{2.3026}{t} \log_{10} \left(\frac{100}{T} \right) \quad (1)$$

where T is the transmittance %, t is the thickness of the crystal (2 mm). In the high photon energy region, the energy dependence of the absorption co-efficient suggests the occurrence of a direct band gap of the crystal obeying the following equation [11].

$$(\alpha h\nu) = A (h\nu - E_g)^{\frac{1}{2}} \quad (2)$$

To calculate the band gap value, Tauc's relation [12] was employed and a graph was plotted between $(h\nu)$ and $(\alpha h\nu)^2$ as shown in Figure 3 (b). The band gap energy for SR method grown crystal was calculated by

extrapolating the straight line portion of the curve to zero absorption and is found to be 5.2 eV, this agree well with the theoretically calculated value 5.3 eV by using the formula ,

$$E_g = \frac{hc}{\lambda_{\max}} eV \quad (3)$$

where h is the Planks constant, c is the velocity of light and λ is the cut-off wavelength (234 nm).As a consequence of a wide band gap, the grown crystal has large transmittance in the entire visible region [13].

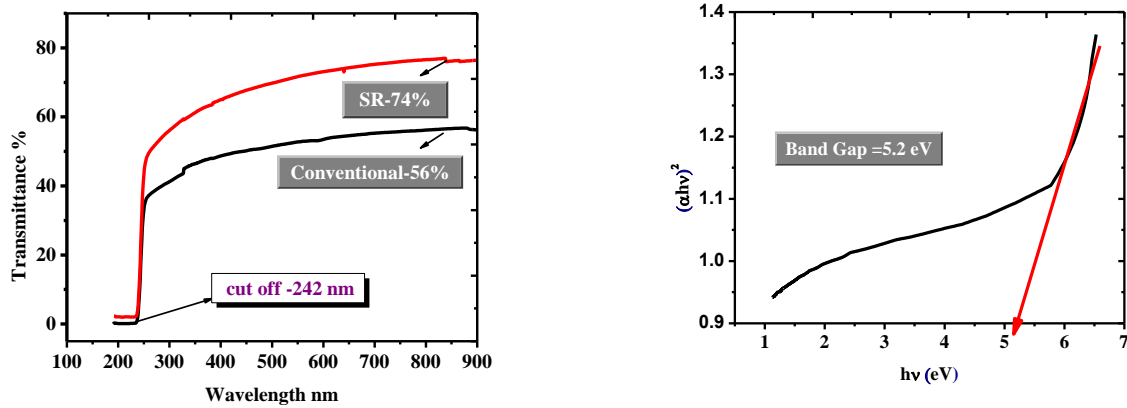


Figure 3 (a) UV-Visible NIR spectrum of MSM crystals

(b) Band gap energy (E_g)

3. Photo Lumescence Measuremet

The photoluminescence study is one of the standard techniques for characterizing single crystals to identify the various electronic energy levels due to excitation. Its intensity also depends on the crystallinity as well as structural perfection of the crystal [14]. The recorded PL spectra in the wavelength range from 250 nm to 700 nm for conventional and SR method grown MSM crystal are shown in Figure 4. For the photo excited wavelength of 250 nm, single emission peak was observed at 488 nm for both the crystals corresponding to blue emission. From the figure it is clear that the high intensity peak exhibited by SR method grown crystal suggest its high crystalline, structural perfection and its suitability for potential applications in optoelectronic devices.

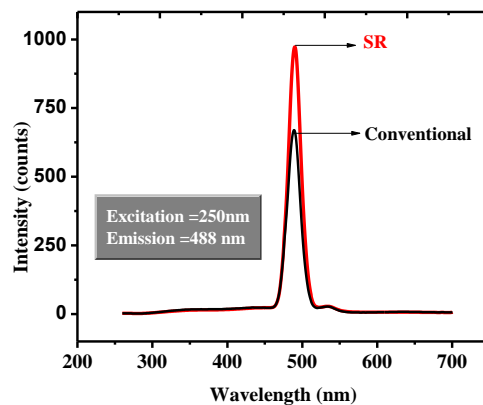


Figure 4 Photoluminescence spectrum of MSM crystals

4. Chemical Etching Analysis

The quality of the crystalline perfection is generally known by the analysis of etch pits on the crystal surface. To study the distribution of structural defects in the grown crystals, chemical etching studies were made on conventional and SR method grown $\langle 101 \rangle$ plane of MSM crystals using water as etchant at room temperature. The conventionally grown MSM crystal was completely immersed into the etchant for 5 s and then taken out immediately. The etchant on the surface was gently wiped using tissue paper and examined under optical microscope. Figure 5 (a) shows the formation of a discrete layer shaped etch pattern on the $\langle 101 \rangle$ plane of conventionally grown MSM crystal and it is also observed that these discrete layers shaped etch pits were obtained due to dislocations caused by different facets, growth sectors and growth sector boundaries [15]. The etch pit density was calculated using the formula,

$$EPD = \frac{\text{Number of etch pits}}{\text{Area}} \quad (4)$$

is found to be $6.5 \times 10^2 \text{ cm}^{-2}$ for conventionally grown crystal. The SR method grown $\langle 101 \rangle$ facet MSM crystal was also subjected for etching studies and compared its etch pit patterns of conventionally grown crystal. Figure 5 (b) shows the definite layer shaped etch pattern. These etch pits were found to be bulky and less number of etch pits compared to conventionally grown crystal. This was due to decrease in dislocation density as defined in morphology $\langle 101 \rangle$ facet growth. As a result the etch pit density (EPD) was found to be $3.7 \times 10^2 \text{ cm}^{-2}$ and lower than that of conventionally grown crystal. This also confirms its systematic packing arrangements and its crystalline perfection. Such observation were also reported on $\langle 100 \rangle$ directed Diglycine zinc chloride dehydrate (DGZC), $\langle 001 \rangle$ directed Triglycine sulphate (TGS) $\langle 101 \rangle$ and $\langle 100 \rangle$ directed KDP single crystals [16-18].

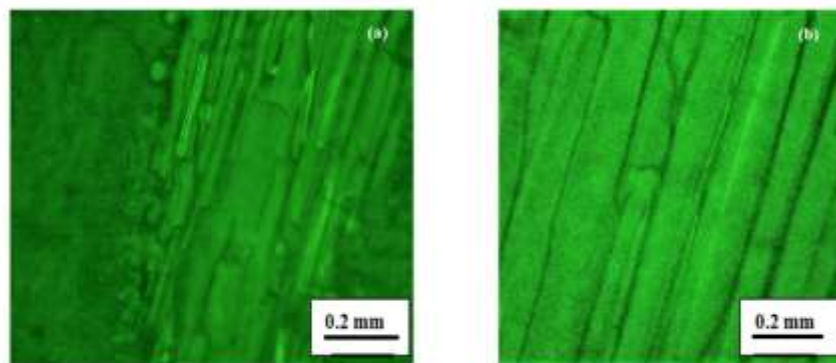


Figure 5 Etching study of MSM crystals grown by (a)conventional and (b) SR method

5. Micro Hardness Measurement

The good quality crystals are needed for device fabrication not only with good optical performance but also with excellent mechanical behavior. Micro hardness testing is one of the best methods of understanding the mechanical properties of materials. Such as fracture behavior, yield strength, brittleness index and temperature of cracking [19-20]. The conventional and SR method grown MSM crystal with $\langle 101 \rangle$ face was employed for Vickers's micro harness studies. Vickers's indentation was made for various loads ranging from 25 to 300 g with a constant indentation time of 10 s for each trial. The mean diagonal length was used to calculate the Vickers's hardness number (H_v) using the formula,

$$H_v = 1.854 \frac{P}{d^2} \text{ Kg} / \text{mm}^2 \quad (5)$$

where P is the applied load (g) and d is the diagonal length. A plot obtained between the hardness value (H_v) and the load (P) for conventional and SR method grown MSM crystal is shown in Figure 6 (a). The trace of Vickers's hardness illustrates a steep rise in hardness number for the load range 25-200 g, which reveals that the grown crystal exhibits reverse indentation size effect (RISE) [21]. The H_v value beyond 200 g load the hardness value decreases and therefore attains a load independent value. Similar kind of behavior is observed for 4-Hydroxy L-Proline (HLP) [22] and L-Glutamic acid hydrochloride (LGHCL) [23]. The maximum H_v value

obtained for conventional and SR method grown MSM crystal are 31.43 kg/mm² and 58.35 kg/mm² respectively for the load 200g. This confirms that the mechanical property of the SR method grown single crystal is better than the conventionally grown MSM crystal. On applying mechanical stress by the indenter; dislocations are generated locally at the region of the indentation and further more measurements are not possible [24]. Apparently the hardness of the SR method grown crystal gained resistance to produce dislocation, thus contributing greater crystalline perfection. The plot between log p versus log d was drawn using Meyers law. The Meyer index number *n* was calculated from the given relation,

$$P = Ad^n \tag{6}$$

which gives the relationship between load P and size d as known by the equation have determined the slope of the plot that is shown in Figure 6 (b). The value of *n* for conventional and SR method grown crystal is 2.9 and 2.4 respectively; suggesting that both belong to soft category according to Onitsch [25].

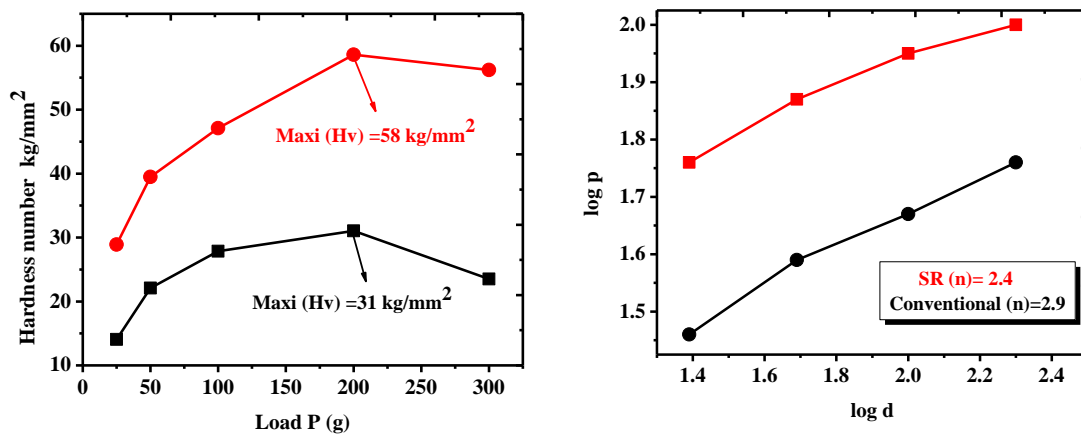


Figure 6 (a) Vickers micro hardness plot of MSM crystal

(b) Meyer index plot of MSM crystal

6. Dielectric Measurement

The capacitance and dissipation factor of the conventional and SR method grown crystals were measured for various frequencies at room temperature in order to expose the dielectric behavior of the grown crystal. Two opposite surfaces across the breadth of conventional and SR method grown samples were treated with silver paste to make it to behave like a parallel plate capacitor. The dielectric constant (ϵ') was calculated from the values of capacitance using the relation

$$\epsilon' = \frac{C_p d}{\epsilon_o A} \tag{7}$$

where *A* is the area of the cross-section of the sample, *d* is the thickness of the sample and ϵ_o is the permittivity of free space (8.854×10^{-12} F/m). Dielectric loss ($\tan \delta$) was also calculated and the variation of the above said parameters with respect to frequency are shown in Figure 7 (a) and (b). It is clear from the figure that the dielectric constant and dielectric loss are found decreasing with increase in frequency for conventional and SR method grown MSM crystals. It is a known fact that the high values of dielectric constant at low frequency and its low value at high frequency are due to the presence and loss of all polarization respectively [26]. The enhanced dielectric constant value for SR method grown crystal than the conventional method may be associated to its perfect crystalline nature. Figure 7 (b) shows that low dielectric loss for SR method grown crystal indicates that the grown crystal contains minimum defects.

On comparison, it is noteworthy to mention that the high dielectric constant and low dielectric loss is obtained for the crystal grown by SR method. These characteristics suggest that it possesses enhanced optical quality with less number of defects.

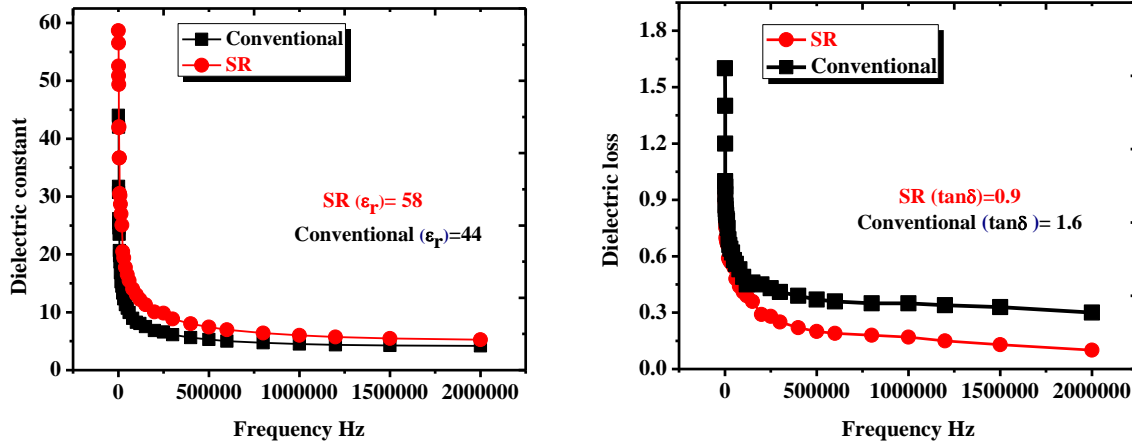


Figure 7 (a) Dielectric constant of MSM crystal

(b) Dielectric loss of MSM crystal

7. Polarizability Parameters

The solid state parameters were calculated to understand the nature of the material in order to analyze the NLO efficiency of the crystal. The valence electron plasma energy, Penn gap, Fermi energy and electronic polarizability by Penn analysis and Clausius –Mossotti equations have been detailed previously [22] which has been calculated for the SR method grown MSM crystal and listed in the Table 1. The calculated solid state parameters of the grown crystal are compared with the standard KDP material. From the above said parameters, it is observed that the values obtained are found to be higher than KDP crystal [27].

Table 1 MSM crystal Electronic polarizability (α) results based on dielectric analysis

Parameters	MSM crystal grown by SR method	Values of KDP
Plasma energy $\hbar\omega_p$ (eV)	24.02	17.33
Penn gap energy E_P (eV)	2.92	2.39
Fermi energy E_F (eV)	30.40	12.02
Electronic polarizability (α) using Penn analysis (cm^3)	4.58×10^{-23}	2.14×10^{-23}
Electronic polarizability (α) using Clausius-Mossotti equation (cm^3)	2.89×10^{-23}	2.18×10^{-23}
Electronic polarizability (α) using optical band gap (cm^3)	2.03×10^{-23}	-

8. Photoacoustic Analysis

[Jayanthi *et al.*,6(10): October, 2017]
ICTM Value: 3.00

The thermal diffusivity is a favorable property for NLO materials during high laser irradiation. A thermal property of the SR method grown MSM crystal was analyzed by using photo acoustic spectrometer. A collimated light from a tungsten filament lamp is focused on the sample which is placed in acoustic free sample cell using a convex lens. The photoacoustic signal is detected by a sensitive microphone and is recorded digitally [22]. MSM crystal of thickness 1.5 mm were polished and further used for the analysis. The plot was drawn between square root of chopping frequency and normalized PA signal for MSM crystal as shown in Figure 8. The thermal diffusivity of the crystal was calculated by curve fitting method adopted by Barros Mela and Faria [28] and the results are listed in Table 2, the thermal diffusivity are derived from the following relations [29]

$$\alpha = f_c l^2 \text{ m}^2 / \text{s} \tag{8}$$

where f_c is the characteristic frequency of the sample and l is the thickness of the sample. The thermal diffusivity of the crystals is $1.44 \times 10^{-6} \text{ m}^2/\text{s}$ and is equal to standard KDP crystal [30].

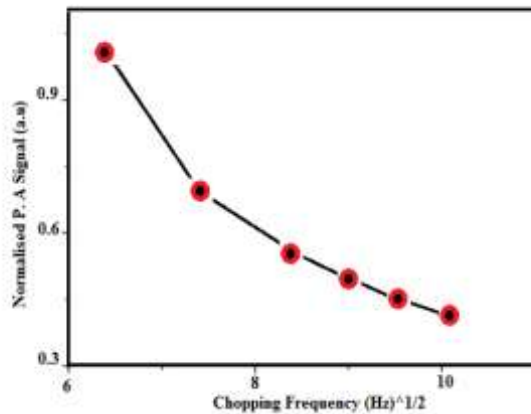


Figure 8 Photo acoustic (PA) plot for the SR method grown MSM crystals

Table 2 Thermal diffusivity for SR method grown MSM crystals

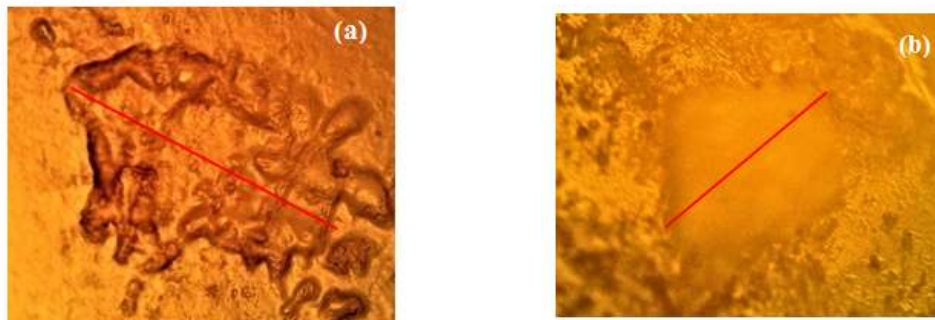
Rf (Hz)	Normalized PA signal amplitude (arb.unit)
	SR method grown MSM crystal
6.24	0.97
7.54	0.66
8.21	0.58
8.94	0.45
9.52	0.41
10.12	0.38
Thickness of the sample in (mm)	1.5
Thermal diffusivity (α)	$1.44 \times 10^{-6} \text{ m}^2/\text{s}$

9. Laser Damage Threshold

For NLO applications, it is essential for the crystal to withstand high power intensities because high optical intensities are involved in nonlinear optical processes. As the choice of a material for NLO application is its optical damage tolerance [31]. To obtain high laser damage threshold, the crystal should possess better crystalline perfection with lesser defects. This experiment was carried out using Q-switched Nd: YAG laser operating at 1064 nm radiation with 8 ns for conventional and SR method and the observed laser damage of the crystals is shown in Figure 9 (a) and (b) respectively. From the apparent damage morphology it can be distinguished that the damaged site area of SR method grown MSM crystal was less than the crystal grown by conventional method. The power density was calculated using the relation

$$\text{Power Density } (P_d) = \frac{E}{\tau \pi r^2} \quad (9)$$

where the energy E is the input energy density (m J), τ is the pulse width (ns) and r is the spot radius (μm) of the beam spot at focal point. The calculated laser damage threshold for the crystal grown by conventional method is 2.9 GW/cm² and for the SR method is 5.0 GW/cm² in relation to 23mJ and 31mJ input energy respectively. The higher laser damage threshold value of SR method grown crystals is due lesser defects.



**Figure 9 Laser damaged surface pattern of MSM crystal for
 (a) Conventional and (b) SR method grown crystal**

10. Thermal Analysis

The thermal stability of the MSM crystal is studied using thermal analysis (TG/DTA). The powdered MSM sample of weight 8.06 mg was analyzed in N₂ atmosphere by using Perkin Elmer Diamond TG/DTA instrument at a heating rate of 10°C/min for a temperature range of 50 °C -850 °C. The TG/DTA curves are shown in Figure 10. From the figure it is clear that the absence of weight loss indicates between 100 °C -175 °C indicates that the compound is stable up to 175 °C. In the DTA curve, an exothermic peak observed around 280 °C can be attributed to the decomposition of the sample and its corresponding weight loss is found to be 93.21 % according to TGA curve.

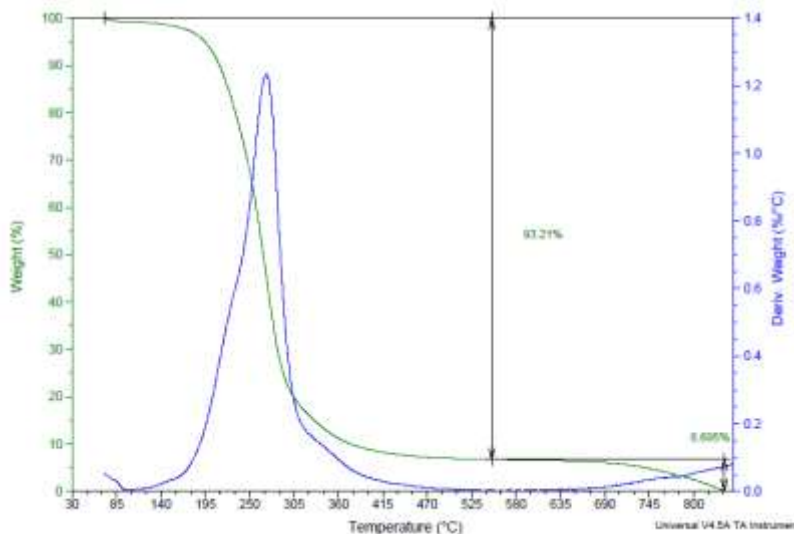


Figure 10 TG-DTA curve of MSM crystal

11. SHG Measurement

The fundamental beam of 1064 nm from Q-switched Nd: YAG laser was used to determine the conversion efficiency of the grown MSM crystal, a standard and familiar method known as powder and Kurtz Perry technique was employed [32]. To measure the SHG efficiency of the MSM crystal, the crystal was granulated and densely packed in a capillary tube that was exposed to laser radiation. A high intensity Q-switched Nd: YAG laser ($\lambda=1064$ nm) with pulse width duration of 10 ns at repetition rate of 10 Hz was focused on the samples by lens. An emission of green light was seen in the sample confirming Second harmonic signal which was detected by photomultiplier tube and displayed on a storage oscilloscope. The second harmonic signal of 34mV was obtained, while the standard KDP crystal gave an SHG signal of 24 mV for the same input energy of 1.5 mJ/ pulse. From the obtained results it was confirmed that the relative SHG efficiency of MSM crystal was 1.4 times that of well known KDP crystal.

V. CONCLUSION

The bulk single crystal of Methane Sulphony Morpholine (MSM) along $\langle 101 \rangle$ plane with the dimension of 65 mm length and 20 mm diameter has been grown successfully by SR method. The grown crystal was subjected to single crystal diffraction analysis, the crystal exhibited orthorhombic system with non-centrosymmetric space group $P2_12_12_1$. Higher transparency and higher hardness values have been achieved in SR method grown crystal compared to crystal grown by conventional method which is also well agreed with etch pit density. The intensity of the emission peak observed in the blue region is high for SR method grown crystal. Dielectric measurements show that the dielectric constant is high and dielectric loss is low in SR method grown crystal compared to the crystal grown by conventional method. The laser damage threshold of SR grown crystal is 1.7 times greater than that of the conventional method grown crystal. The thermal diffusivity of the SR method grown crystal is equal to standard KDP crystal. From TG/DTA analysis it reveals that the crystal is stable up to 175 °C. The SHG efficiency of the crystal was found to be 1.4 times greater than that of KDP. The above results confirmed the suitability of SR method grown crystal for SHG and optoelectronic devices. Table 3 shows the overall comparative investigation of MSM crystals.

Table 3 Comparative investigations of conventional and SR method grown MSM crystal

S. No	Characterization of MSM crystal	Conventional method	SR method
1	Crystal size	6×3×2 mm ³	60 mm in length and 20 mm diameter
2	UV-Visible NIR transmittance	56 %	74 %
3	Photoluminescence (PL) intensity	630 (counts)	880 (counts)
4	Etch pit density (EPD)	6.5×10 ³ cm ⁻²	3.7×10 ³ cm ⁻²
5	Hardness number	31.43 (kg/mm ²)	58.35 (kg/mm ²)
6	Work hardening coefficient (n)	2.9	2.4
7	Dielectric constant at 1 MHz	44	58
8	Dielectric loss at 1 MHz	1.6	0.9
9	Thermal diffusivity	-	1.44×10 ⁻⁶ m ² /s
10	Laser damage threshold values	2.9 (GW/ cm ²)	5.0 (GW/ cm ²)
11	Second harmonic generation (SHG)	-	1.4 times > KDP

VI. ACKNOWLEDGEMENTS

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